

Process for preparing HSiCl₃ by catalytic hydrodehalogenation of SiCl₄

The invention relates to a process for preparing trichlorosilan (HSiCl₃) by catalytic hydrodehalogenation of silicon tetrachloride (SiCl₄) in the presence of hydrogen.

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SiCl₄ and HSiCl₃ are formed together in many industrial processes in silicon chemistry. It is therefore necessary to convert these two products into one another and thus meet the respective demand for one of the products.

- 10 Furthermore, high-purity HSiCl₃ is an important starting material in the production of solar silicon.

Various catalysts and the process for converting SiCl₄ to HSiCl₃ in the presence of hydrogen have been known for a long time.

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Thus, EP 0 658 359 A2, for example, discloses a process for the catalytic hydrodehalogenation of SiCl₄ to HSiCl₃ in the presence of hydrogen, in which finely divided transition metals or transition metal compounds selected from the group consisting of nickel, copper, iron, cobalt, molybdenum, palladium, platinum, rhenium,

- 20 cerium and lanthanum are used as unsupported catalysts, these are able to form silicides with elemental silicon or silicon compounds. Problems are, as a result of the strongly endothermic nature of the reaction, the indirect introduction of the heat of reaction and the sintering of the catalyst particles, associated with a drop in activity. In addition, separation of the used finely divided catalysts from the product mixture
25 represents a considerable expense.

It is an object of the present invention to provide a further possible way of producing HSiCl₃ by catalytic hydrodehalogenation of SiCl₄.

According to the invention, this object is achieved as set forth in the claims.

It has surprisingly been found that a degree of conversion [conv. = $100 \% \cdot c(HSiCl_3)/c_0(SiCl_4)$] in the vicinity of the thermodynamic conversion can be achieved in a simple and economical way when an $SiCl_4/H_2$ mixture is passed over a metal or metal salt which is based on at least one element of main group 2 of the Periodic Table of the Elements and forms stable metal chlorides under the reaction conditions and this catalytic reaction is appropriately carried out at a temperature of from 300 to 1 000°C, preferably from 600 to 950°C, in particular from 700 to 900°C. The use of a metal component selected from the group consisting of Ca, Ba and Sr and their salts is particularly advantageous. The catalytically active system can also have been applied to a support. Preference is in this case given to stable microporous supports, but, for example, not exclusively those based on SiO_2 , in particular low-aluminum zeolites or leached glass. The metal content on the support is advantageously from 0.1 to 10% by weight. For example, the present process can advantageously be carried out in a heatable fixed-bed reactor or moving-bed reactor, but also in a heatable fluidized-bed reactor. $HSiCl_3$ can be isolated from the resulting gaseous product mixture by targeted, i.e. at least partial, condensation. However, the gaseous product mixture can also be used further directly, for example in an esterification process with an alcohol, in a hydrosilylation, in the preparation of pyrogenic silica, in the preparation of monosilane or solar silicon, to name only a few examples.

In particular, the present process avoids toxic heavy metals as catalysts component and reduces sintering of the catalyst, and achieves a relatively high mechanical strength.

In addition, the catalyst systems used according to the invention generally display an above-average stability in respect of deactivation.

The present invention accordingly provides a process for preparing $HSiCl_3$ by catalytic

hydrodehalogenation of SiCl_4 in the presence of hydrogen, in which at least one metal or metal salt selected from among the elements of the main group 2 of the Periodic Table of the Elements (PTE) is used as catalyst at a temperature in the range from 300 to 1 000°C.

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Preference is given to using calcium, strontium, barium, calcium chloride, strontium chloride, barium chloride or mixtures of at least two of the abovementioned components as catalyst in the process of the invention.

- 10 This catalyst can be used as such, for example in a piece or from coarsely crystalline to pulverant as salt having a preferred average particle diameter of from 0.01 to 3 mm, in particular a d_{50} of from 0.05 to 3 mm, as determined by methods known per se, or as supported catalyst.
- 15 It can be advantageous to use the catalyst applied to a support from the group consisting of low-aluminum zeolites, leached glass, for example fused silica, activated carbon, porous siliceous supports or SiO_2 supports.

- 20 Such a supported catalyst system is appropriately based on a microporous support having a pore volume of from 100 to 1 000 mm^3/g and a BET surface area of from 10 to 500 m^2/g , preferably from 50 to 400 m^2/g . The pore volume and the BET surface area can be determined by methods known per se. The support can have the support forms known per se, for example powder, granules, tablets, pellets, extradites, trilobes, spheres, beads, tubes, cylinders, plates, honeycombs, to name only a few examples.
- 25 Such supports preferably have a geometric surface area of from 100 to 2 000 m^2/m^3 or a bulk density of from 0.1 to 2 kg/l , preferably from 0.2 to 1 kg/l .

The catalytically active material can be applied to such a support in a manner known

per se; for example, it is possible to dissolve a metal salt in a suitable solvent, impregnate the support with the solution by dipping or spraying, dry it and, if appropriate, subject to a thermal after-treatment. As solvent, it is possible to use, for example, water, aqueous solutions or alcohols, and it is possible to use salts which on 5 subsequent thermal treatment of the impregnated support, if appropriate in the presence of H₂ and/or HCl, forms stable alkaline earth metal chlorides. Nonlimiting examples of salts which can be used are alkaline earth metal chlorides, alkaline earth metal hydroxides, alkaline earth metal carbonates and alkaline earth metal nitrides. The ready-to-use supported catalyst should appropriately be free of water and oxygen and 10 also not liberate these substances on heating. A supported alkaline earth metal catalyst can be obtained, for example under protective gas, by bringing a support into contact with molten alkaline earth metal and subsequently cooling it. Application of the metal to the support can be carried out under reduced pressure, so that the molten metal can also penetrate into the pore system of the support after the pressure is increased. 15 When such metal catalysts are employed in the process of the invention, they are generally converted into the corresponding stable, catalytically active chloride under the reaction conditions.

The supported catalysts used in the process of the invention preferably have a catalyst 20 content, calculated as element, of from 0.1 to 10% by weight. Particular preference is given to catalyst contents of from 1 to 8% by weight, based on the supported catalyst.

In the process of the invention, it is advantageous to bring an SiCl₄/H₂ mixture having a molar ratio of from 1:0.9 to 1:20 into contact with the catalyst. Particular preference is 25 given to using SiCl₄/H₂ mixtures having a molar ratio of from 1:1 to 1:10, very particularly preferably from 1:1.5 to 1:8, in particular those having a molar ratio of from 1:2 to 1:4. Last but not least, the SiCl₄ used here and the hydrogen, generally of high to very high quality, must be free of hydrogen or hydrogen compounds for safety reasons.

In the process of the invention, the reaction is preferably carried out in a fixed-bed reactor or in a fluidized-bed reactor or a moving-bed reactor.

- 5 It is appropriate to use a reactor whose walls or interior surfaces of the walls comprise a heat-resistant glass, in particular fused silica, a heat-resistant glaze or a heat-resistant ceramic or specialist ceramic. Furthermore, the materials used for the reactor should be largely chemically resistant toward the components present in the process of the invention.

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The catalytic reaction of the invention is preferably carried out at a temperature in the range from 600 to 950°C, particularly preferably from 700 to 900°C, and a pressure of from 0.1 to 100 bar abs., preferably from 1 to 10 bar abs., in particular from 1.5 to 2.5 bar abs.

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To carry out the reaction of the invention, the present process is appropriately operated at a space velocity (SV = volume flow/catalyst volume) of from 2 000 to 30 000 h⁻¹, preferably from 5 000 to 15 000 h⁻¹. The gas mixture in the reactor appropriately has a linear velocity (LV = volume of flow/cross-sectional area of the reactor) of from 0.01 to

20 10 m/s, preferably from 0.02 to 8 m/s, particularly preferably from 0.03 to 5 m/s. The volume flows on which the reaction-kinetic parameters mentioned above and below are based are in each case at STP. In process engineering terms, the reaction of the invention is appropriately carried out in the turbulent range.

- 25 In general, the process of the invention is carried out as follows:

A heatable reactor which is largely resistant to elevated temperatures and chlorosilanes or HCl is generally firstly dried, for example by baking, filled with dry, O₂-free protective

gas, for example argon or nitrogen, and charged with catalyst under protective gas. The catalyst is generally preconditioned in a stream of H₂ at elevated temperatures up to the reaction temperature. However, the catalyst can also be preconditioned under an atmosphere or stream of HSiCl₃, SiCl₄, H₂/HSiCl₃, H₂/SiCl₄ or H₂/HSiCl₃/SiCl₄.

- 5 Preconditioning of the catalyst is appropriately carried out for from 0.1 to 12 hours, preferably from 2 to 6 hours, at a temperature above 300°C. If an alkaline earth metal as such is used as catalyst, the preconditioning under said conditions can be carried out by heating it over a period of from about 0.5 to 4 hours to a temperature below the melting point of the alkaline earth metal used and keeping it at this temperature for from
10 about 1 to 10 hours. The temperature can then be increased to the desired operating temperature and the process of the invention can be carried out, with the respective catalyst particles generally retaining their original shape. The reactor can appropriately be monitored under operating conditions by means of at least one thermocouple and at least one flow measurement device.

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To prepare a feed mixture, it is possible to convert SiCl₄ into the gas phase, add the appropriate proportions of hydrogen and feed it to the reactor which is at operating temperature.

- 20 The product mixture obtained at the outflow end can be used directly as feed stream in a further process or can be worked up to isolate HSiCl₃, for example by condensation. Amounts of hydrogen or SiCl₄ obtained in this way can advantageously be recycled. The product stream from the outlet end of the reactor, i.e. before further utilization or work-up, can also be conveyed in countercurrent through a heat exchanger at the inlet
25 end of the reactor in order to preheat the feed stream before it enters the reactor and thus to make an advantageous energy saving.

However, the catalyst can also be used in the form of a fluidized bed, in which case a

cyclone is appropriately located at the outlet end of the reactor to separate off the catalyst or supported catalyst. The catalyst collected in this way can advantageously be recirculated to the reactor.

- 5 In the process of the invention, the reaction product obtained, i.e. product mixture, can be worked up or processed further. Preference is given to (i) fractionally or at least partially condensing the product mixture in a manner known per se, isolating liquid, advantageously highly pure HSiCl_3 and recirculating any hydrogen or silicon tetrachloride obtained to the feed stream to the present process or (ii) advantageously
- 10 passing the product stream as starting material to a direct further use.

The present invention is illustrated by the following examples without being restricted thereby.

15 **Examples:**

Example 1

- 20 ZSM 5 is impregnated with a 0.1 N BaCl_2 solution, subsequently dried and ignited at 450°C under a hydrogen atmosphere for 1 hour. 10% by weight of salt is applied in this way.

In a fused silica reactor having a diameter of 15 mm and a length of 250 mm, 1.3 g of this zeolite containing metal salt are installed on a frit. Heating is effected electrically by 25 means of a tube furnace to 845°C. An H_2/SiCl_4 mixture flows through the reactor at a throughput of 7 l/h. The conversion achieved in the reaction is monitored by gas chromatography. Table 1 reports the degree of conversion of SiCl_4 into HSiCl_3 at various molar ratios of $n(\text{H}_2)/n(\text{SiCl}_4)$.

Table 1

$n(H_2)/n(SiCl_4)$	Degree of conversion into $HSiCl_3$ (%)
4	17.4
5	19.2
6	20.7
8	23.2

Example 2

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The fused silica reactor described in example 1 is used. 1 g of metallic barium having a mean particle diameter 1.5 mm is used as solid and is preconditioned ($H_2/HSiCl_3$ atmosphere, heating at 700°C for 2 hours, hold at 700°C for 2 hours (presumably the formation of $Ba/BaSi_x/BaCl_2/Si$ phases), heating to operating temperature). The degrees of conversion are determined as a function of the reaction temperature at a volume flow of 7 l/h and a constant $n(H_2)/n(SiCl_4)$ ratio of 6:1.

Table 2

Temperature (°C)	Degree of conversion of $HSiCl_3$ (%)
800	13.8
825	17.9
845	21.8

Example 3

The fused silica reactor described in example 1 is used. 1 g of anhydrous SrCl_2 having a mean diameter of 0.7 mm is used as solid. The degrees of conversion are determined
5 as a function of the reaction temperature at a volume flow of 7 l/h and a constant $n(\text{H}_2)/n(\text{SiCl}_4)$ ratio of 6:1.

Table 3

Temperature (°C)	Degree of conversion of HSiCl_3 (%)
800	15.4
825	17.2
845	19.2